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COMPLETE SPECIFICATION

Improvements in or relating to the Treatment of Cellulosic Textile Fabrics

We, HEBERLEIN AND CO., A.G., a Swiss Body Corporate, of Wattwil, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with processes for improving the wet and dry crease resistances of cellulosic textile fabrics. The term cellulosic textile fabric is used herein to mean fabrics composed wholly or partly of fibres of cellulose or cellulose derivatives.

It has been proposed to improve the dry crease recovery of cellulosic textile fabrics, especially cotton fabrics by treating them with synthetic resin pre-condensates, preferably with methylol substituted ureas, urea derivatives and melamines. The treatment comprises simply impregnating the cellulosic fabric with the pre-condensate so that it penetrates into the cellulose fibres and then heating the fabric to temperatures between 130° C and 180° C in the presence of a catalyst, so that the pre-condensate is converted into an insoluble resin by polycondensation in and around the fibres and/or by reacting with the cellulose to form cross links.

It has also been proposed to impregnate cellulosic fabrics with a cross-linking agent for cellulose, e.g. dichloropropanol, and subsequently to treat the fabric with alkali or to apply a cross-linking agent, such as formaldehyde, acetals or methylol compounds of nitrogen compounds such as ethylene urea or melamine. This process gives a fabric having a good wet crease recovery but the dry crease recovery is almost unaffected.

British Patent Specification No. 504,916 describes a process for imparting to textile material of natural or regenerated cellulose a water or wear resisting shape wherein the textile material is impregnated with swelling agents, more particularly with zinc chloride solution, and simultaneously or subsequently —if desired with intermediate rinsing—is treated with formaldehyde, then partially dried and subjected to a shaping by embossing or other pressing operation and finally subjected to hot fixing and completely dried.

It has now been found that by treating cellulosic textile fabrics, especially cotton fabrics, with a solution containing as a swelling agent for cellulose a salt in certain selected concentrations and also containing a cellulose cross-linking agent and subsequently heating the fabric, a particularly good wet crease recovery and dry crease angle can be achieved.

According to the present invention therefore there is provided a process for treating a cellulosic textile fabric as herein defined for the improvement of the wet and dry crease resistances thereof which comprises impregnating the fabric with an aqueous solution containing from 5 to 40 percent by weight of a salt as a swelling agent for cellulose and a cellulose cross-linking agent and subsequently heating the fabric at a temperature of at least 100° C whereby the wet and dry crease resistances of the fabric are improved. It is probable that cross linking of the cellulose with bridge formation takes place while the cellulose is at least partially swollen. To complete the finishing of the fabric, the fabric may then be finally washed and dried in usual manner.

The heating is preferably carried out for from 1 to 10 minutes at temperatures of from 100 to 150° C, and may for example be effected directly after the impregnation with the aqueous salt solution containing the cellulose cross-linking agent. Alternatively

[Price 4s. 6d.]

after the impregnation the fabric may be first dried by warming at temperatures of 50 to 100° C before the main heating is carried out.

Swelling agents for cellulose, which are suitable for use in the process of this invention include aqueous solutions of metal salts, particularly zinc chloride as well as zinc thiocyanate, calcium thiocyanate, lithium bromide and magnesium perchlorate. The aqueous solution contains from 5 to 40 per cent by weight of the cellulose swelling agent.

Suitable cross-linking agents for the cellulose are those which, with or without the at an elevated temperature to cross link cellulose.

The cross linking agent may for example be one of the so-called reactant resins which do not form any resins in the conventional sense but react with the hydroxyl groups of addition of an acid or alkaline catalyst, react the cellulose thus forming cross links. Reactant resins which may be used as the cellulose cross linking agent in the process of this invention include the following classes of compounds:— acetals, (e.g. reaction products of formaldehyde and diethylene glycol), dimethylol monocarbamates (e.g. dimethylolmethyl carbamate), dimethylol ureas and cyclic dimethylol ureas (e.g. dimethylol ethylene urea), dimethylol propylene urea and dimethylol dihydroxyethylene urea), triazones (such as 1,3-dimethylol-5-hydroxy-ethyl-perhydrotriazone-2), methylol melamine compounds (such as tetramethylol melamine), water soluble etherified methylol melamine compounds and epoxides (such as the diglycidyl ether of ethylene glycol). Aldehydes for example formaldehyde, glyoxal, and glutaraldehyde may also be used as cross linking agents. Further examples of cross linking agents include epichlorhydrin, the reaction products of pyridine with chloromethyl ethers, divinylsulphone derivatives, tris(1-aziridinyl)-phosphineoxide and 1,6-di(ethyleneiminocarbonamido)-*n*-hexane.

Optionally the usual acid or potentially acid catalysts, may also be added to the impregnating solution. Examples of such catalysts include oxalic acid, citric acid, magnesium chloride, zinc fluoborate, magnesium perfluoborate, ammonium sulphate and zinc nitrate. In certain cases, for example with the use of divinylsulphone derivatives as cross-linking agents, alkaline catalysts, such as sodium carbonate are used.

The textile fabric is preferably treated, either before or after the treatment with the swelling agent impregnating solution with a softening agent e.g. a cation-active or substantive, or ketene type softener. If the softening agent used is soluble in the impregnating solution, then it can be incorporated therein. The impregnated textile fabric may also be calendered either before or after the main heating step.

The process according to the invention can in general be applied to textile fabrics consisting wholly or partly of cellulosic fibres. Thus, for example it may be applied to woven, non-woven or knitted fabrics of natural cellulose fibres, such as cotton, or regenerated cellulose fibres or fibres of cellulose derivatives. Blended fibre fabrics containing cellulose fibres mixed with other natural or synthetic fibres can also be treated.

The invention will now be illustrated by the following examples:

In all the following examples, an imitation cotton poplin was used which had been mercerised and bleached according to common practice and which had the following fabric construction and crease recovery properties:

Ends and picks per 1/4 French inch - warp 34 weft 17
Yarn number English: - - - - warp 40 weft 30

Crease recovery angle of the mercerised and bleached fabric:

Mean value of warp and weft, dry: 47°
" " " " " " wet: 63°

The determinations of the crease angles were carried out as follows: test strips 5 cm long (warp) and 3 cm wide (weft) were cut on the straight from the fabric. These strips were conditioned by keeping them for 24 hours at 21° C and 65% relative humidity. The strips were then placed upon a clean microscope slide and a part of the strip bent upwardly through 180° parallel to the narrow side at a distance of 1cm from the end of the strip. The strip was then covered with a further microscope slide and loaded for 1 hour with a weight of 1 kg. Finally the test strips were placed in an air conditioned room on a glass plate and after a recovery time of a quarter of an hour the angles formed by the folded strips were measured. This angle is taken as the dry crease angle. For every test several strips were cut out in both directions of the fabric and creased as above and the mean value for the dry crease angle taken.

For measuring the wet crease angle, the strips were placed, prior to the creasing, for 10 minutes at room temperature in water to which 1 g. of a wetting agent per litre, e.g., Erkantol (Farbenfabriken Bayer) had been added, the excess water was then lightly wiped off and the strip then tested as in the determination of the dry crease angle.

EXAMPLE 1

The fabric was impregnated with an aqueous solution containing per litre,

Zinc chloride, - - - - - - 150 g.
50% Dimethylol methyl carbamate sodium - - - - - - - 140 cc.

All surplus moisture was squeezed out and the fabric was then heated under tension in both the warp and weft directions for two minutes at 120° C, rinsed with cold water, briefly washed at 60° C in a bath containing 1 g of lauryl sulphonate and 1 g of sodium carbonate per litre, rinsed again with cold water, squeezed off and dried under tension. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry 88°
" " " " " " wet 131°

Example 2

The fabric was impregnated with an aqueous solution containing per litre:

Zinc chloride - - - - - - 250 g
50% of Dimethylol methyl carbamate solution - - - - - 140 cc.

All surplus moisture was squeezed out and the fabric was then dried by warming under tension in both the warp and weft directions at 75° C, and then heated for two minutes at 130° C, rinsed with cold water, briefly washed at 60° C in a bath containing 1 g of lauryl sulphonate and 1 g of sodium carbonate, rinsed again with cold water and then dried under tension. The resulting fabric had the following crease angles;

Mean value of warp and weft, dry: 121°
" " " " " " wet: 158°

Example 3

The treatment was effected as described in Example 2 except that the impregnating solution used contained per litre.

Zinc chloride - - - - - - 200 g
50% Dimethylol methyl carbamate solution - - - - - - - 140 cc
"Aquapel" 380 (a ketene softening agent sold by Hercules Powder Co. The word "Aquapel" is a registered Trade Mark) 20 g

and after drying, the fabric was heated for two minutes at 125° C. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry 127°
" " " " " " wet 152°

Example 4

The treatment was effected as described in Example 2 except that the impregnating aqueous solution used contained per litre:

Zinc chloride - - - - - - 200 g.
40% formaldehyde solution - - 150 cc.

and after the drying the fabric was heated for two minutes at 140° C. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry 156°
" " " " " " wet 163°

Example 5

The treatment was effected as described in Example 2 except that the impregnating aqueous solution used contained per litre:

Calcium thiocyanate trihydrate - 350 g
50% Dimethylol propylene urea solution - - - - - - - 140 cc
Catalyst PR (=zinc nitrate) of Ciba, Basle - - - - - - 14 g

and after drying, the fabric was heated for three minutes at 150° C. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry 74°
" " " " " " wet 145°

Example 6

The fabric was impregnated with an aqueous solution containing per litre

Magnesium perchlorate - - - 150 g
50% Dimethylol propylene urea solution - - - - - - - 150 cc
Catalyst PR - - - - - - 15 g

All surplus moisture was squeezed out and the fabric was then heated without any intermediate drying step, for six minutes at 140° C and subsequently heated as described in Example 1. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry 129°
" " " " " " wet 155°

Example 7

The fabric was impregnated with an aqueous solution, containing per litre:

Zinc thiocyanate - - - - - 150 g
"Fixapret TN" - - - - - 160 g

(a triazone resin sold by Badische Anilin- and Sodafabric, Ludwigshafen. The word "Fixapret" is a registered Trade Mark), All surplus moisture was then squeezed out and the fabric was dried by warming at a temperature of 100° C. The fabric was then heated for four minutes to 130° C and finished as described in Example 2. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry 110°
" " " " " " wet 136°

Example 8

The treatment was effected according to Example 2 except that the impregnating aqueous solution used contained per litre:

Zinc chloride - - - - - - 200 g
30% Glyoxal solution - - - 160 cc

After drying the fabric by warming at 75° C, it was then heated for 2½ minutes at 140° C. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry 152°
" " " " " " wet 154°

Example 9

The fabric was impregnated with an aqueous solution containing per litre:

Zinc chloride - - - - - - 150 g
"Cassurit MKF" - - - - - 80 g

(a melamine-formaldehyde pre-condensate sold by Casella Farwerke Mainkur. The

word "Cassurit" is a registered Trade Mark).

All surplus moisture was then squeezed out and the fabric was dried by warming at 90° C, heated for three minutes at 140° and finished as described in Example 2. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry	131°
" " " " " " wet	136°

EXAMPLE 10

The fabric was impregnated with an aqueous solution containing per litre:

Zinc chloride - - - - - -	200 g.
Quaker Reactant - - - - -	100 g.

(a modified glycolacetal sold by Quaker Chemical Products Corp.).

All surplus moisture was removed by squeezing and the fabric was then dried by warming at 90° C. The fabric was then heated for 2 minutes at 160° C and finished as described in Example 2. The resulting fabric had the following crease angles:

Mean value of warp and weft, dry	69°
" " " " " " wet	130°

EXAMPLE 11

The fabric was impregnated with an aqueous solution containing per litre:

Lithium bromide - - - - -	150 g
Tris (1-aziridinyl) phosphine-oxide	100 g
Zinc boronfluoride - - - -	4 g

All surplus moisture was removed by squeezing and the fabric was then dried by warming at 80° C heated for 4 minutes at 140° C and finished as described in Example 2.

As compared to the starting material, the resulting fabric had increased dry and wet crease angles.

WHAT WE CLAIM IS:—

1. A process for treating a cellulosic textile fabric as herein defined for the improvement of the wet and dry crease resistances thereof which comprises impregnating the fabric with an aqueous solution containing from 5 to 40 per cent by weight of a salt as a swelling agent for cellulose and a cellulose cross-linking agent and subsequently heating the fabric at a temperature of at least 100° C whereby the wet and dry crease resistance of the fabric are improved.

2. A process as claimed in claim 1, in which the heating is carried out for 1 to 10 minutes at a temperature of 100 to 150° C.

3. A process as claimed in claim 1 or claim 2, in which the textile fabric is subjected prior to the heating to drying at a temperature of 50 to 100° C.

4. A process as claimed in any of the preceding claims in which the cross-linking agent used is a reactant resin.

5. A process as claimed in claim 4, in which the reactant resin used is dimethylol methyl carbamate.

6. A process as claimed in claim 4, in which the reactant resin used is a dimethylol compound of ethylene or propylene urea.

7. A process as claimed in any of claims 1 to 3, in which the cross-linking agent used is an aldehyde.

8. A process as claimed in claim 7 in which the cross-linking agent used is formaldehyde.

9. A process as claimed in any of the preceding claims in which the swelling agent for cellulose used is an aqueous solution of a metal salt.

10. A process as claimed in claim 9, in which the metal salt used is zinc chloride.

11. A process as claimed in claim 9 in which the metal salt is zinc thiocyanate, calcium thiocyanate, lithium bromide or magnesium perchlorate.

12. A process as claimed in any of the preceding claims in which the aqueous solution contains an acid or alkaline catalyst.

13. A process as claimed in any of the preceding claims in which the textile fabric is treated before, during or after the impregnating step with a softening agent.

14. A process as claimed in claim 13, in which the softening agent is soluble in the impregnating solution and incorporated therein.

15. A process as claimed in any of the preceding claims in which the textile fabric is calendered before or after the heating step.

16. A process as claimed in claim 1 substantially as herein described with reference to the foregoing examples.

17. Cellulosic textile fabrics whenever treated by a process as claimed in any of the preceding claims.

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